ACYL-PLATINUM(II) AND -PALLADIUM(II) COMPLEXES DERIVED FROM 2-HYDROXYBENZALDEHYDE DERIVATIVES. X-RAY STRUCTURE OF [Pt(OC6H4CO)(P(p-CH3C6H4)3)2]

C. ANKLIN, P.S. PREGOSIN *,

Laboratorium für Anorganische Chemie, ETH-Zentrum, Universitätstrasse 6, CH-8092 Stazione, Roma (Italy)

F. BACHECHI, P. MURA and L. ZAMBONELLI

Istituto di Strutturistica Chimica, "G. Giacomello", CNR, CP 10, I-00016 Monterotondo Stazione, Roma (Italy)

Summary

Platinum(II) and palladium(II) complexes containing chelating acyl ligands have been synthesized from salicylaldehyde, 2-hydroxynaphthaldehyde and 2-hydroxy-3-methoxybenzaldehyde. The platinum(II) complexes [Pt(acyl)L$_2$], acyl = OC$_6$H$_4$CO, OC$_{10}$H$_6$CO, O(m-CH$_3$OC$_6$H$_3$CO), L = tertiary phosphine, 1/2 diphenylphosphinoethane, can be isolated with both monodentate and chelating diphosphines, whereas for palladium only the compounds with chelating phosphines are readily obtainable. The reactions of [Pt(OC$_6$H$_4$CO)L$_2$] with HCl afford *trans*-[PtCl(OHC$_6$H$_4$CO)L$_2$], L = monodentate tertiary phosphine and *cis*-[PtCl(OHC$_6$H$_4$CO)L$_2$], L$_2$ = 1,2-bis-diphenylphosphinoethane, in which the metal—carbon bond remains intact. The structure of [Pt(OC$_6$H$_4$CO)-(P(p-CH$_3$C$_6$H$_4$)$_3$)$_2$] has been determined by X-ray diffraction methods and found to have the expected square planar structure. Some relevant bond lengths and angles are: Pt—P; 2.271(4) and 2.348(5) Å; Pt—C; 1.96(2) Å and Pt—O; 2.07(1) Å; P—Pt—P = 101°, C—Pt—O = 82°.
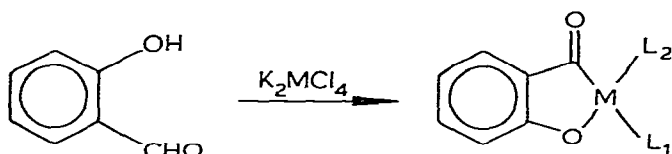
Introduction

An acyl transition metal complex is now recognized to be a key intermediate in the homogeneously catalysed hydroformylation reaction [1]. The steps which lead to this type of molecule are now well known and both theoretical [2] and synthetic [3—6] studies have shown that the insertion of carbon monoxide into a metal—carbon bond is a crucial step. There are several other

possible routes to acyl derivatives and these include oxidative addition of an acyl halide by a complex containing the metal in a low oxidation state [7,8] (e.g. reaction of RCOX with PtL_4 [9] or reaction of a small cluster with an aldehyde [10]. Several groups [10,11,12] have studied the activation of organic aldehydes by transition metals, since there is a potential interest in terms of a) new synthetic routes to organic molecules and b) mechanistic detail related to hydroformylation chemistry as the transformation:

$$M + R{-}CHO \rightarrow HM{-}C\overset{\displaystyle O}{\underset{\displaystyle R}{\big\langle}}$$
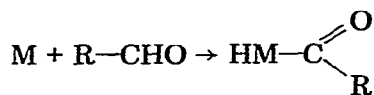
is the reverse of the product forming step.

We have found that K_2PtCl_4 activates salicylaldehyde, (2-hydroxybenzalde-

hyde) so that complexes of the form $[Pt(OC_6H_4)L_2]$, may be obtained in high yield, L = a variety of phosphine, arsine and nitrogen ligands [13]. We report here an extension of this chemistry to include a) new salicylaldehyde derivatives of both palladium(II) and platinum(II) and b) the structure of $[Pt(OC_6H_4CO)(P(p\text{-}CH_3C_6H_4)_3)_2]$ as determined by X-ray diffraction methods.

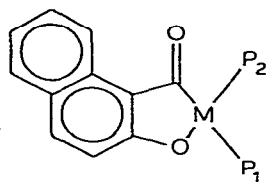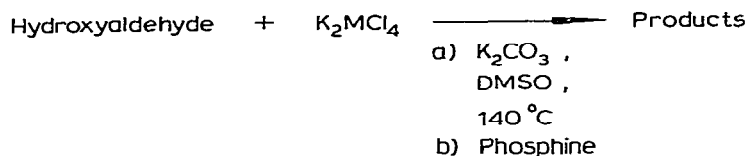## Results and discussion

1. Synthesis and characterization

Like salicylaldehyde, the ligands 2-hydroxynaphthaldehyde and 2-hydroxy-
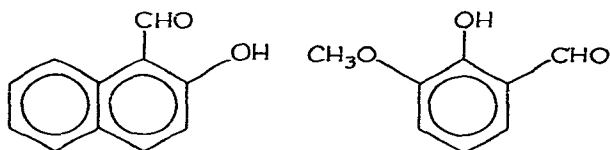
3-methoxybenzaldehyde react as shown in scheme 1, and give the acyl complexes I—VIII in good yield (62—95%).

The complexes were isolated as yellow solids, with the exception of IV, which was obtained as a yellow oil, and gave satisfactory microanalyses (see Table 1). All of these phosphine compounds afford $^{31}P\{^1H\}$ NMR spectra containing two doublets due to the non-equivalent spins P_1 and P_2 and the appropriate ^{195}Pt satellites ($I = 1/2$, natural abundance = 34%) for the complexes of this metal. The magnitude of the values $^2J(P_1P_2)$ is consistent with a *cis* orientation of the two phosphorus spins [14], and the values $^1J(^{195}Pt, {}^{31}P)$ are comparable with those found in related compounds [13]. The coupling constant data, along with the phosphorus chemical shifts, $\delta(^{31}P)$, are given in Table 2. The assignment of P_1 and P_2 in the platinum derivatives follows directly from the known dependence of $^1J(^{195}Pt, {}^{31}P)$ on the nature of the *trans* ligand

SCHEME 1

Hydroxyaldehyde   +   K₂MCl₄ ————————► Products
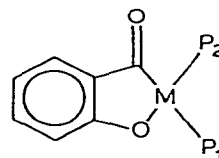
        a) K₂CO₃ ,
           DMSO ,
           140 °C
        b) Phosphine

(I) Pd , diphos

(II) Pt , diphos

(III) Pd , Ph₂PCH═CHPPh₂

(IV) Pt , PEt₃
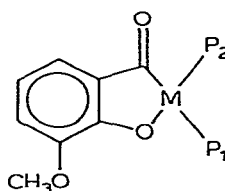
(V) Pd , diphos

(VI) Pt , diphos

(VII) Pd , diphos

(VIII) Pd, Ph₂PCH═CHPPh₂

[14,15,16]. For the palladium compounds the interpretation is less certain and we base our assignment on previously developed empirical correlations of ^{31}P chemical shifts in palladium complexes [17,18]. Additional support for the proposed structures comes from ^{1}H NMR spectroscopy. The most obvious features here are the absence of an aldehyde proton resonance and, for Ph₂PCH₂-CH₂PPh₂, a complex four proton grouping arising from the nonequivalent methylene groups.

The aromatic region of these ^{1}H spectra are complicated by the presence of the strong absorptions due to the PPh₂ moiety; however, a complete analysis of the acyl fragment has proven possible for the complex IV and for the two

TABLE 1

ANALYTICAL AND IR DATA

| Complex	Yield (%)	Analysis found (calcd.) (%)			IR(ν(CO)) [a]
		C	H	P	
I [b]	80	63.98(65.84)	4.49(4.48)		1630
II [c]	62	58.18(18.19)	4.01(3.96)		1594
III	95				1632
IV	62	45.60(45.90)	6.12(6.03)	10.4(10.3)	
V	92	63.07(62.34)	4.78(4.62)	9.6(9.5)	1638
VI [b]	62	52.71(54.91)	4.07(4.20)	8.6(8.3)	1608
VII [b]	82	61.91(63.42)	4.52(4.52)	9.3(9.9)	1630
VIII [d]	79	62.63(63.62)	4.51(4.21)	9.9(10.0)	1640
XI [e]	95	60.56(61.28)	5.10(4.93)	6.43(6.45)	
XII	60	56.14(56.10)	3.85(3.80)		1610
XIII	61	53.55(53.37)	4.12(3.62)		1615

[a] As KBr pellets, in cm^{-1}. [b] These acyl complexes show a tendency to lose CO when heated. Consequently, the % C found is often slightly too low. [c] Molecular weight (osmometric in CH₂Cl₂): 769 (764). [d] Molecular weight (osmometric CH₂Cl₂) 586 (623). [e] Cl: 4.26 (3.69) %.

TABLE 2

^{31}P{^{1}H} NMR DATA ^{a} FOR THE ACYL COMPLEXES

| Complex	$\delta(P_1)$	$\delta(P_2)$	$^2J(P_1,P_2)$	$^1J(^{195}Pt,^{31}P_1)$	$^1J(^{195}Pt,^{31}P_2)$
I	20.3	41.6	29		
II	36.0	29.8	10	1424	4364
III	24.4	40.5	7		
IV	12.8	13.8	10	1397	4239
V	22.5	44.8	32		
VI	37.5	30.7	9	1496	4254
VII	22.9	45.3	31		
VIII	27.9	44.2	10		
XI	19.9			3238	
XII	18.0			3207	
XIII ^{b}	19.9			3220	
XIV ^{b}	16.2			3196	

^{a} Data are for CDCl$_3$ solutions at room temperature: coupling constants are in Hz, chemical shifts in ppm relative to external H$_3$PO$_4$. A positive sign indicates a low field (high frequency) shift. ^{b} In CH$_2$Cl$_2$/CD$_2$Cl$_2$.

methoxy derivatives V and VI. In all the naphthyl complexes H(8) (δ 8.62—
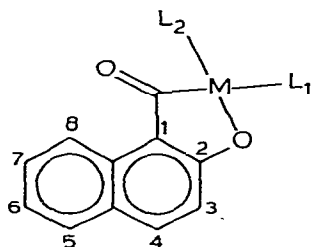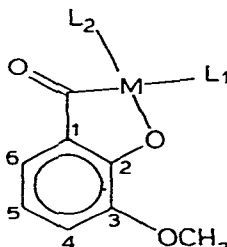
(IV) (V ,VI)

9.04 ppm) resonates at much lower field than the remaining protons. For 2-hydroxynaphthaldehyde this signal appears at δ 8.20 ppm, and therefore the complexation of the aldehyde carbon induces a substantial low field shift of this proton. Presumably the rigid nature of the acyl chelate prevents carbonyl rotation, thus fixing the nearly H(8) in a deshielding region of the carbonyl bond. A summary of the proton NMR data may be found in Table 3.

We have successfully isolated yellow palladium intermediates which we believe have the composition [Pd(OC$_6$H$_4$CO)L$_1$L$_2$]$^-$, [Pd(OC$_{10}$H$_6$CO)L$_2$L$_2$]$^-$, L$_1$ = Cl, L$_2$ = DMSO, as sodium and potassium salts, respectively. The proton NMR data for these complexes, IX and X, are in reasonable agreement with those for I—VIII.

Reaction of IX and X with Ph$_2$PCH$_2$CH$_2$PPh$_2$ affords the more readily purified compounds I and VII and confirms our previous suggestion that step b in Scheme 1 is of secondary importance in terms of the activation of the aldehyde. Indeed with K$_2$PdCl$_4$ and DMSO as solvent, the reaction temperature plays a critical role. At 100°C, with triphenylphosphine as ligand, we obtained a 51% yield of the phenolate complex trans-[Pd(OC$_6$H$_4$CHO)(PPh$_3$)$_2$] as its mono DMSO solvate ($\delta(^{31}$P) = 19.2, $\delta(^1$H) = 9.83 for CHO; IR: ν(CO) = 1650

TABLE 3

SOME ^{1}H NMR DATA [a] FOR THE COMPLEXES

| Complex		H(3)	H(4)	H(5)	H(6)	H(7)	H(8) [b]
IV	δ	6.68	7.25	7.29	6.75	7.00	8.90
	J	$H_3, H_4 = 9.0$		$H_5, H_6 = 8.2$	$H_6, H_7 = 6.9$	$H_7, H_8 = 8.6$	
				$H_5, H_7 = 1.7$			
V [c]	δ		6.77	6.22	6.69		
	J		$H_4, H_5 = 7.7$	$H_5, H_6 = 7.1$			
			$H_4, H_6 = 1.6$				
VI [d]	δ		6.77	6.31	6.85		
	J		$H_4, H_5 = 7.3$	$H_5, H_6 = 7.9$			
			$H_4, H_6 = 1.5$				
IX	δ	7.18	7.61 [e]	7.61 [e]	7.10	7.34	8.52
	J	$H_3, H_4 = 9.4$	$H_4, H_5 = 7$			$H_7, H_8 = 9.0$	

[a] CDCl$_3$ solutions at room temperature. [b] δ(H(8)) for I—III = 8.66, 9.04 and 8.62 ppm, respectively. In acetone-d_6. [c] OCH$_3$ = δ 3.83 ppm; assignment H(4) and H(6) is tentative. [d] OCH$_3$ = δ 3.93 ppm; assignment H(4) and H(6) is tentative. [e] H(4) and H(5) have very similar chemical shifts. Measured in acetone-d_6.

cm^{-1}). This observation supports our earlier supposition that deprotonation of the phenol oxygen and subsequent substitution precede attack at the aldehyde carbon.

Although we have successfully prepared platinum acyl complexes with both chelating and monodentate phosphines, the palladium complexes with PPh$_3$ and PEt$_3$ ligands afford stable yellow solids of a different composition. Preliminary evidence (see Experimental) suggests that these are acyl compounds with only one PPh$_3$ ligand, which are dynamic on the NMR time scale at room temperature. Low temperature ^{31}P measurements in the presence of an excess of PPh$_3$ reveal that [Pd(OC$_6$H$_4$)(PPh$_3$)$_2$] can be generated in situ: δ(^{31}P) = 35.6, 11.5, ^2J(P$_1$P$_2$) = 32 Hz; however, these acyl complexes are considerably more labile than their platinum analogs.

2. Reactivity

To gain further insight into the nature of the acyl—metal bond we have treated several of our complexes with gaseous HCl. In CHCl$_3$, [Pt(OC$_6$H$_4$CO)-(P(p-XC$_6$H$_4$)$_3$)$_2$], X = H, CH$_3$ both react to give >90% yields of the compounds *trans*-[PtCl(OHC$_6$H$_4$CO)(P(p-XC$_6$H$_4$)$_3$)$_2$], X = H (XI), CH$_3$ (XII) as yellow crystalline materials. The phenol oxygen is protonated and no longer coordinated whereas the acyl carbon is still bound. The *trans* geometry is indicated by the single ^{31}P resonance (e.g. for XI δ(^{31}P) = 19.9, ^1J(^{195}Pt, ^{31}P) = 3238 Hz), whereas the presence of a platinum—chloride bond is suggested by new bands in the IR at 275 cm^{-1} and 280 cm^{-1} for XI and XII, respectively. For [PtCl(OHC$_6$H$_4$CO)(PPh$_3$)$_2$] metathesis reactions lead smoothly to the corresponding *trans*-bromide (XIII) and -iodide (XIV) complexes. An interesting feature of the ^{1}H spectrum of XII concerns the phenolic proton which appears at δ 11.15 ppm. This somewhat unusual chemical shift probably derives from a structure such as XV which has the proton bound to both oxygens via a hydrogen bond. In support of this we observe a coupling constant of 6 Hz between the phenolic proton and platinum. The complexes [M(OC$_6$H$_4$CO)(diphos)],

(XV)

R = p-CH$_3$C$_6$H$_4$
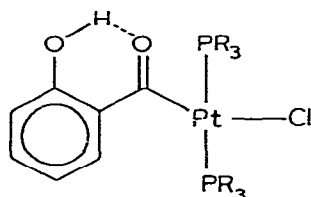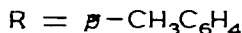
M = Pd, Pt, also react with HCl to afford the analogous chloro(acyl) complexes. These seem more reactive, perhaps as a result of the *trans* disposition of acyl and phosphorus ligands, and further work on them is in progress. All the platinum acyl—metal bonds seem relatively resistant to cleavage by HCl.

3. X-ray structure of [Pt(OC$_6$H$_4$CO)(P(p-CH$_3$C$_6$H$_4$)$_3$)$_2$]

In view of the general interest in acyl complexes as well as the relative stability of the platinum—acyl bond, we felt it worthwhile to determine the structure of one of our chelating acyl compounds, and found the salicylaldehyde tri-*p*-trolyl phosphine derivative to be suitable.

The crystal structure consists of discrete molecules of complex and disordered molecules of CHCl$_3$. Figure 1 shows a perspective view of the molecule indicating the atom numbering scheme used. A selection of bond lengths and angles is reported in Table 4.

The coordination around the platinum atom is square-planar, with the two phosphine ligands in the expected *cis* positions and the salicylaldehyde residue acting as a chelate ligand complexing through the phenolic oxygen and the aldehyde carbon atoms. There are only small deviations of the atoms involved in platinum—ligand binding from the calculated least-squares plane through these atoms. Significant deviations from the regular angles of the square-plane are found in the observed bond angles about platinum, partially as a result of the small chelate bite of the salicylaldehyde residue [O(1)—Pt—C(7) = 82.1(6)°] and partly due to the two bulky P(p-CH$_3$C$_6$H$_4$)$_3$ ligands [P—Pt—P = 101.0(2)°].

The two Pt—P bond distances [2.271(4) and 2.348(5) Å] differ significantly (~17σ). The longer Pt—P(2) bond, *trans* to C(7), indicates the stronger *trans*-influence of carbon compared with oxygen. Similar results have been observed in the complexes *cis*-[PtCl(3-chloro-1,1,3,3-tetrafluoropropan-2-one)-(PPh$_3$)$_2$] Pt—P = 2.247(5) and 2.362(5) Å [19], *cis*-[PtF{CH(CF$_3$)$_2$}(PPh$_3$)$_2$], Pt—P = 2.218(7) and 2.310(7) Å [20] and 3,3,4-tricyano-2,2,-bis(triphenylphosphine)-1-oxa-2-platinacyclobutane Pt—P = 2.247(6) and 2.311(6) Å [21] all of which contain *cis* PPh$_3$ ligands, a carbon ligand and a fourth ligand of much smaller *trans* influence. Differences of 0.07—0.10 Å are generally reported between Pt—P bond distances *trans* to carbon [22] and those *trans* to oxygen [23]. The Pt—C(7) bond distance of 1.96(2) Å is comparable with values of 1.95 to 2.06 Å found for other Pt—C(sp^2) distances [24—27], and in excellent agreement with X-ray data for palladium and platinum acyl complexes (see Table 5). The Pt—O(1) bond distance of 2.07(1) Å is in the range
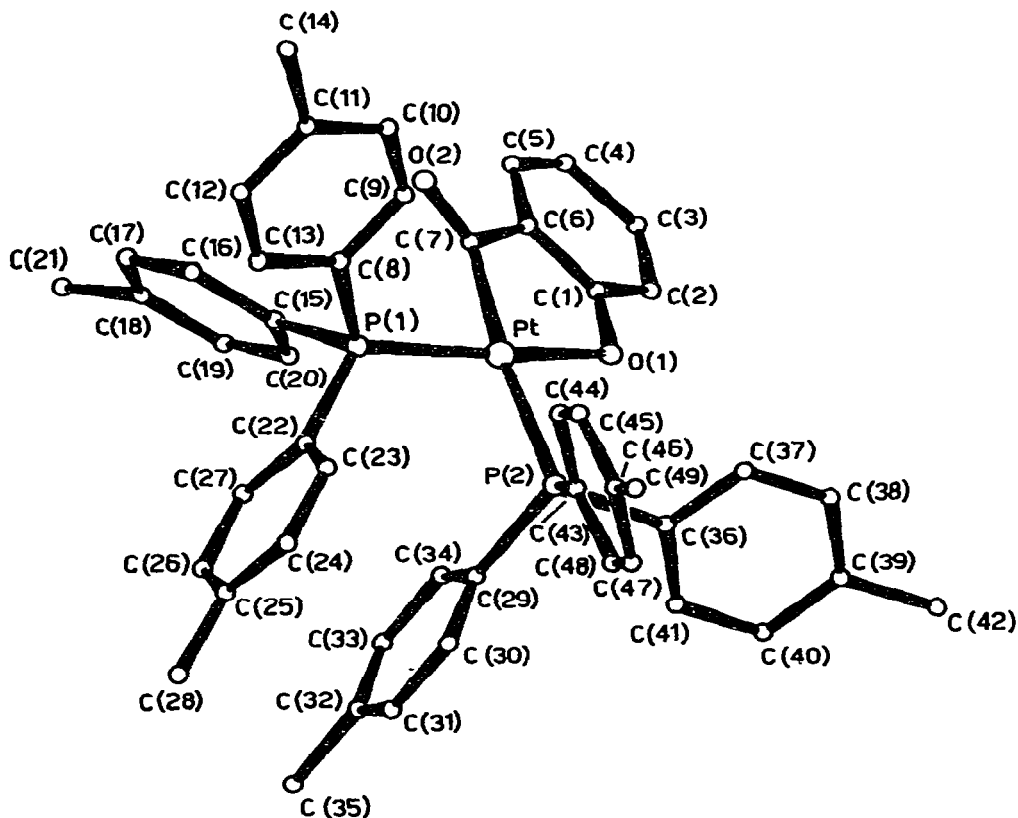
Fig. 1. Structure of [Pt(OC$_6$H$_4$CO)(P(p-CH$_3$C$_6$H$_4$)$_3$)$_2$].

TABLE 4

SELECTED BOND LENGTHS (Å) AND ANGLES (°)

Pt—P(1)	2.271(4)	P(1)—Pt—P(2)	101.0(2)
Pt—P(2)	2.348(5)	P(1)—Pt—C(7)	87.4(4)
Pt—C(7)	1.96(2)	P(1)—Pt—O(1)	164.7(3)
Pt—O(1)	2.07(1)	P(2)—Pt—C(7)	171.6(4)
C(6)—C(1)	1.39(3)	P(2)—Pt—O(1)	89.4(4)
C(6)—C(7)	1.47(2)	C(7)—Pt—O(1)	82.1(6)
C(1)—C(2)	1.40(2)	Pt—C(7)—O(2)	132.6(12)
C(1)—O(1)	1.37(2)	Pt—C(7)—C(6)	113.7(14)
C(2)—C(3)	1.35(3)	O(2)—C(7)—C(6)	113.0(18)
C(3)—C(4)	1.41(4)	Pt—O(1)—C(1)	109.5(10)
C(4)—C(5)	1.41(3)	C(6)—C(1)—C(2)	119.4(18)
C(5)—C(6)	1.38(3)	C(6)—C(1)—O(1)	120.5(13)
C(7)—O(2)	1.20(3)	C(2)—C(1)—O(1)	120.0(19)
		·C(1)—C(2)—C(3)	119.9(23)
		C(2)—C(3)—C(4)	122.0(18)
		C(3)—C(4)—C(5)	117.7(21)
		C(4)—C(5)—C(6)	120.2(22)
		C(5)—C(6)—C(1)	120.8(15)
		C(5)—C(6)—C(7)	126.7(19)
		C(1)—C(6)—C(7)	112.3(17)

TABLE 5

RELEVANT BOND LENGTHS IN ACYL COMPLEXES

Compound	Distance (Å)		
	M—C	C—O	Ref.
[Pt₂(μ-Cl)₂(COEt)₂(PMe₂Ph)₂]	1.972(5)	1.208(7)	29
[PtCl₂(CONPr½)CO]⁻	1.96(2)	1.36(3)	30
trans-[PdCl(COPrⁿ)(PPh₃)₂]	1.974(10)	1.210(11)	31
[PdCl(COCH₂CH(R)NEt₂)(NHEt₂)]	1.95(1)	1.13(2)	32
[Pt(OC₆H₄CO)(P(p-CH₃C₆H₄)₃)₂]	1.96(2)	1.20(3)	this work

observed for other Pt—O distances, but it is longer than usually found in salicyl-aldehyde derivatives, in which Pd—O and Pt—O bond lengths fall in the range 1.90—2.00 [23,28].

Apart from the aryl groups the molecule is roughly planar, and the salicylaldehyde moiety has fairly regular geometry. Interestingly, the acyl carbon—oxygen bond lengths, 1.20 Å, is similar to those in [Pt₂(μ-Cl)₂(COEt)₂(PMe₂Ph)₂], 1.208(7) Å [29] and trans-[PdCl(COPrⁿ)(PPh₃)₂] 1.210(11) Å [31], which, in turn resemble normal conjugated carbon—oxygen double bond distances (~1.207(6) [33]). The phosphine ligands have distorted tetrahedral geometry, with the Pt—P—C and C—P—C angles averaging 114.8(4) and 105.1(5)°, respectively. The six P—C distances, as well as the six C—CH₃ distances in the tolyl groups, are not significantly different from one another and average 1.841(10) and 1.53(2) Å, respectively.

The geometry of the solvent CHCl₃ molecule, which is disordered in two distinct positions, is of limited accuracy (mean values of 1.72 Å and 111° are found for the C—Cl distances and Cl—C—Cl angles).

Conclusions

Our results show that palladium and platinum acyl complexes are obtainable in good yield from salicylaldehyde derivatives. For Pd^{II} the chelating nature of both the acyl and tertiary phosphine ligands seem to contribute to the stability of the complex. The most basic site in terms of attack by HCl seems to be the coordinated oxygen, and in support of this we find a rather long Pt—O distance in the solid state. The square planar molecular structure of the complex is maintained both in the solid and solution, and there seem to be no unusual strains within the molecule. Indeed the Pt—CO distance is quite normal. Given the inertness of the platinum—carbon bond towards H⁺ it will be interesting to see if these molecules behave like organic ketones.

Experimental

Crystal data

Yellow crystals of [Pt(OC₆H₄CO)(P(p-CH₃C₆H₄)₃)₂] were obtained by slow evaporation of a CHCl₃ solution. A disordered molecule of CHCl₃ per molecule of complex was found during the X-ray analysis. A summary of crystal data is given in Table 6.

TABLE 6

CRYSTAL DATA

Formula	$C_{50}H_{47}Cl_3O_2P_2Pt$	
Formula-Wt.	1043.32	
Cell constants [a]	$a = 11.888(3)$ Å	$\alpha = 105.84(2)°$
	$b = 14.306(5)$ Å	$\beta = 90.35(2)°$
	$c = 16.360(3)$ Å	$\gamma = 109.33(3)°$
	$V = 2511(1)$ Å^3	
Space group	$P\bar{1}$ (triclinic, $Z = 2$)	
Density (g cm^{-3})	1.380 (calc.), 1.385 (10) (exper.) [b]	
$\mu(Cu$-$K_\alpha)$ (cm^{-1})	76.68	

[a] Determined by least-squares from the measured angular positions of 15 reflections. [b] Measured by flotation in ZnI_2 solution.

Intensity measurement

Intensities were measured with an automatic diffractometer Syntex P2$_1$, using graphite-monochromated Cu-K_α radiation ($\theta_{max} = 58°$, ω-scan range = $1.0°$). The processed data were corrected for the usual factors and for the shape anisotropy effect. Of the unique data collected 5473 independent reflections with $I > 3\sigma(I)$ were used in the subsequent analysis.

Structure analysis and refinement

The structure was solved by the heavy atom method and refined by least-squares to a final R of 0.076 ($R_w = 0.086$). The fixed contribution of the hydrogen atoms, geometrically positioned, was included in the last cycles during which all the heavier atoms but those of the tolyl rings were allowed to vibrate anisotropically.

The refinement was carried out with a six-blocks approximation of the normal-equation matrix; the function minimized was $\Sigma\omega(|F_o| - |F_o|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$. Phenyl rings were refined as rigid groups (D_{6h} symmetry, C—C = 1.392 Å). Scattering factors and anomalous dispersion terms were taken from International Tables for X-ray Crystallography [34]. The calculations were performed with local programs on the UNIVAC 1100/20 computer of the University of Rome and on the HP 21MS minicomputer of the CNR Research Area.

Bruker WM-250 and HX-90 spectrometers were used for the NMR measurements. ^1H and ^{31}P NMR spectra were measured as CDCl$_3$ solutions for I—III, V—VIII and XI—XIV. The ^1H spectra of IV, IX and X were measued in acetone-d_6. For IX and X this is necessary due to their poor solubility in CDCl$_3$ whereas for IV we chose to avoid the problem of potential overlap of the CHCl$_3$ signal by using acetone. Chemical shifts are in ppm (± 0.1 for ^{31}P, ± 0.01 for ^1H) and coupling constants are in Hz (± 3 Hz for ^{31}P, ± 0.6 for ^1H). IR spectra were measured as KBr pellets using a Beckmann IR 4250. Microanalyses were performed by the microanalytical Laboratory of the ETH Zürich.

The three aldehydes were purchased from Fluka AG, Buchs, Switzerland. Na$_2$PdCl$_4$ and K$_2$PdCl$_4$ were prepared from PdCl$_2$ (Johnson-Matthey) and a stoichiometric amount of the appropriate chloride salt. The chelating phosphines were commercially available from STREM Chemicals, USA.

Preparation of [Pd(OC₁₀H₆CO)(diphos)] (I)

A stirred solution of Na₂PdCl₄ (0.200 g, 0.679 mmol) in 10 ml DMSO at 100°C was treated sequentially with Na₂CO₃ (0.216 g, 2.04 mmol) and 2-hydroxy-1-naphthaldehyde (0.117 g, 0.679 mmol). The temperature was raised to 140°C, maintained at this point for 0.5 h and then reduced to 100°C at which time solid diphos (0.270, 0.679 mmol) was introduced. Further cooling to 60°C was followed by removal of the solvent under vacuum. The residue was extracted with methylene chloride, and the filtered extract treated with active charcoal, filtered again, and finally concentrated to give the product as a deep-yellow powder (0.367 g, 80% yield).

The same method was employed for complexes II, III, V and VI using the appropriate potassium (instead of sodium) tetrahalide complex.

Preparation of the anionic complexes Na[Pd(OC₆H₄CO)Cl(DMSO) (IX) and K[Pd(OC₁₀H₆CO)Cl(DMSO)] (X)

The same preparation procedure was employed as for I, except that the mixture was cooled directly from 140 to 60°C, and that, after solvent removal, extraction was carried out with acetone. Filtration was followed by concentration to give the product. From Na₂PdCl₄ (0.200 g, 0.679 mmol) and salicylaldehyde (0.083 g, 0.679 mmol) we obtained 0.200 g of IX (81% yield) as a yellow powder. From K₂PdCl₄ (0.250 g, 0.613 mmol) and 2-hydroxy-1-naphthaldehyde (0.106 g, 0.613 mmol) we obtained 0.115 g of X (43% yield) also as a yellow solid.

Synthesis of the palladium salicylaldehyde complex with PPh₃

An identical procedure to that used for the synthesis of I was employed. From Na₂PdCl₄ (200 mg, 0.613 mmol), salicylaldehyde (75 mg, 0.613 mmol) and PPh₃ (322 mg, 1.226 mmol) we obtained a yellow powder (0.293 g, 64%) whose NMR characteristics were consistent with a complex having the coordinated acyl ligand and one PPh₃. The compound is either a mixture of isomers or impure, and we find two signals in the ³¹P NMR spectrum, δ 38.7 and 39.1 ppm. The microanalytical data found: C, 60.5; H, 4.25; P, 5.78; Cl, 0.09% are consistent with Pd(OC₆H₄CO)(PPh₃), C₂₉H₁₉O₂PPd calcd.: C, 61.6; H, 3.9; P, 6.4%. The solution molecular weight is 841 (calcd. for Pd(OC₆H₄CO)(PPh₃) is 487). It is possible that the complex is dimeric, with bridging oxygen atoms.

Acknowledgements

References

1 G.W. Parshall, J. Molecular Catal., 4 (1978) 243.
2 H. Berke and R. Hoffmann, J. Amer. Chem. Soc., 100 (1978) 7224.
3 F. Calderazzo, Angew. Chem., 89 (1977) 305.
4 P.E. Garrou and R.F. Heck, J. Amer. Chem. Soc., 98 (1976) 4115.
5 N. Sugita, J.V. Minkiewicz and R.F. Heck, Inorg. Chem., 17 (1978) 2809.
6 G. Booth and J. Chatt, J. Chem. Soc. A, (1966) 634.
7 D.R. Fahey and J.E. Mohan, J. Amer. Chem. Soc., 99 (1977) 250.
8 M.A. Bennett and J.C. Jeffrey, Inorg. Chem., 19 (1980) 3763.

9   C.D. Cook and G.S. Jauhal, Canad. J. Chem., 45 (1967) 301.

10 K. Azam, A.J. Deeming and I.P. Rothwell, J. Organometal. Chem., 178 (1979) C20.

11 K. Azam, A.J. Deeming and I.P. Rothwell, J. Chem. Soc. Dalton, (1981) 91.

12 T. Rauchfuss, J. Amer. Chem. Soc., 101 (1979) 1045.

13 H. Motschi, P.S. Pregosin and H. Ruegger, J. Organometal. Chem., 193 (1980) 397.

14 P.S. Pregosin and R.W. Kunz in P. Diehl, E. Fluck and R. Kosfeld (Eds.), NMR Basic Principles and Progress, Vol. 16, Springer-Verlag Berlin, 1979 and references therein.

15 A. Pidcock, R.E. Richards and L.M. Venanzi, J. Chem. Soc. A, (1966) 1707.

16 F.H. Allen, A. Pidcock and C.R. Waterhouse, J. Chem. Soc. A, (1970) 2087.

17 S.O. Grim and R.L. Keiter, Inorg. Chim. Acta, 4 (1970) 56.

18 G. Balimann and P.S. Pregosin, J. Magn. Reson., 22 (1976) 235.

19 D.R. Russell and P.A. Tucker, J. Chem. Soc. Dalton, (1975) 2222.

20 J. Howard and P. Woodward, J. Chem. Soc. Dalton, (1973) 1840.

21 M. Lenarda, N. Bresciani Pahor, M. Calligaris, M. Graziani and L. Randaccio, J. Chem. Soc. Dalton, (1978) 279.

22 R. Ros, M. Lenarda, N. Bresciani Pahor, M. Calligaris, P. Delise, L. Randaccio and M. Graziani, J. Chem. Soc. Dalton, (1976) 1937.

23 W. Back, E. Leidl, M. Kembler and U. Nagel, Chem. Ber., 113 (1980) 1790.

24 E.M. Badley, J. Chatt, R.L. Richards and G.A. Sim, Chem. Commun. (1969) 1322.

25 D.J. Cardin, B. Cetinkaya, M.F. Lappert, L. Manojlovic Muir and K.W. Muir, Chem. Commun., (1971) 400.

26 W.M. Butler, J.H. Enemark, J. Parks and A.L. Balch, Inorg. Chem., 12 (1973) 451.

27 M.B. Butler and J.H. Enemark, Inorg. Chem., 12 (1973) 540.

28 H. Motschi, C. Nussbaumer, P.S. Pregosin, F. Bachechi, P. Mura and L. Zambonelli, Helv. Chim. Acta, 63 (1980) 2071; A. Chakravorty, Coord. Chem. Rev., 13 (1974) 1.

29 G.K. Anderson, R.J. Cross, L.M. Muir, K.W. Muir and T. Solomun, J. Organometal. Chem., 170 (1979) 385.

30 D.B. Dell'Amico, F. Calderazzo and G. Pelizzi, Inorg. Chem., 18 (1979) 1165.

31 R. Bardi, A. Del Pra, A.M. Piazzesi and L. Toniolo, Inorg. Chim. Acta, 35 (1979) L345.

32 L.S. Hegedus, O.P. Anderson, K. Zetterberg, G. Allen, K. Siirala-Hansen, D.J. Olsen and A.B. Packard, Inorg. Chem., 16 (1977) 1887.

33 International Tables for X-ray Crystallography, Vol. 3, Kynoch Press, Birmingham, England 1968, p. 276.

34 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, England, 1974, Tables 2.3B and 2.3.1.